

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY AND THE RESEARCH LABORATORIES, K-25 PLANT, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

## Thermodynamic Properties of Technetium and Rhenium Compounds. IV. Low Temperature Heat Capacity and Thermodynamics of Rhenium<sup>1</sup>

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RECEIVED JULY 20, 1953

The low temperature heat capacity of metallic rhenium has been measured from 20–300°K. by adiabatic calorimetry. The molal entropy was calculated to be  $8.89 \pm 0.03$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> at 298.16°K.

### Introduction

The heat capacity of metallic rhenium has been measured by adiabatic calorimetry from 20 to 300°K. and the molal entropy and thermodynamic functions have been calculated. The entropy was determined to permit the calculation of entropies of formation for rhenium compounds and also as a guide for estimating the same property for corresponding technetium compounds. With this determination, niobium remains the only other stable element of the transition metals for which this thermodynamic function is not available.

### Experimental

**Material.**—The metallic rhenium was furnished by the University of Tennessee and was used as received. The metal had been prepared by the reduction of ammonium perrhenate at 500–600° in hydrogen, sintered at 1000° and allowed to cool in hydrogen. Experience has demonstrated that metal prepared in this manner is 99.9% pure. Although the reduction process initially forms a very finely divided pyrophoric powder, the sintering at high temperatures produces much larger particles (*ca.* 200 mesh). Effects due to particle size on the thermodynamic functions are, therefore, probably absent. The corrected mass of metal used was 61.4995 g. (*in vacuo*).

**Apparatus.**—The adiabatic calorimeter has been previously described<sup>3</sup> and was used without modification. The calorimeter proper was constructed of copper and contained horizontal copper fins at 2-mm. intervals to provide for rapidly attaining thermal equilibrium. This calorimeter, which was gold plated, was one previously calibrated and used for potassium perrhenate.<sup>4</sup> The metal was introduced through a hole (0.5 in.) in the top and sifted down through the fins. The hole was then sealed with a copper plug using soft solder. The calorimeter and its contents were evacuated through an auxiliary copper tube opening for 5–6 hours. During this process the filled calorimeter was flamed and flushed with dry helium. It was then filled to  $\sim 1/3$  atm. with dry helium at room temperature before sealing.

Liquid and solid hydrogen were used as refrigerants below 70°K. and liquid and solid nitrogen from 60°K. up to room temperature. Since the copper calorimeter and incorporated heater and thermohm accounted for about  $2/3$  to  $3/4$  of the heat capacity at low temperature, the values reported below 40° are consequently less accurate than the 0.2% error estimated for the measurements at the higher temperatures.

### Experimental Results

The experimental heat capacity data are given in Table I, and the smoothed thermodynamic values in Table II. The calorie has been taken as 4.1840 absolute joules.

Jaeger and Rosenbohm<sup>5</sup> have determined the

(1) This work was performed for the Atomic Energy Commission.  
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(3) G. D. Oliver and J. W. Grisard, *THIS JOURNAL*, **73**, 1888 (1951).

(4) J. W. Cobble, G. D. Oliver and W. T. Smith, Jr., paper V, *ibid.*, **75**, 5786 (1953).

(5) F. M. Jaeger and E. Rosenbohm, *Proc. Acad. Sci. Amsterdam*, **36**, 786 (1933).

TABLE I

#### EXPERIMENTAL HEAT CAPACITIES OF METALLIC RHENIUM

Atomic weight, 186.31; 0°C. = 273.16°K.

$T_m$ , °C.	$C_p$	$T_m$	$C_p$	$T_m$	$C_p$
20.39	0.158	70.82	3.136	164.92	5.511
22.00	.203	75.39	3.332	173.88	5.583
24.89	.315	77.39	3.466	183.64	5.768
28.80	.454	80.05	3.563	193.20	5.708
31.74	.624	84.00	3.735	202.65	5.802
34.66	.800	92.88	4.117	211.97	5.889
39.98	1.085	103.04	4.396	222.30	5.962
43.96	1.457	112.19	4.662	233.62	5.986
48.89	1.803	121.82	4.884	244.81	6.083
53.82	2.151	131.01	5.056	255.86	6.086
55.42	2.248	139.85	5.202	266.79	6.123
62.26	2.730	148.41	5.323	(277.59	6.183) <sup>a</sup>
66.27	2.845	156.76	5.438	288.30	6.153
				300.01	6.150

<sup>a</sup> High value probably due to traces of moisture.

TABLE II

#### THERMODYNAMIC FUNCTIONS FOR RHENIUM

$T$ , °K.	$C_p$	$S^0$	$\frac{(H^0 - H_0^0)}{T}$	$-\frac{(F^0 - H_0^0)}{T}$
20	0.146	0.049	0.037	0.012
25	.316	.096	.072	.024
30	.541	.173	.131	.042
35	.820	.277	.209	.068
40	1.147	.407	.305	.102
45	1.508	.563	.419	.144
50	1.885	.741	.547	.194
60	2.520	1.143	.824	.319
70	3.084	1.575	1.107	.468
80	3.569	2.020	1.386	.634
90	3.963	2.463	1.644	.819
100	4.305	2.899	1.893	1.006
120	4.843	3.735	2.343	1.392
140	5.197	4.511	2.728	1.783
160	5.459	5.223	3.054	2.169
180	5.648	5.878	3.332	2.546
200	5.804	6.480	3.570	2.910
220	5.936	7.038	3.778	3.260
240	6.041	7.559	3.963	3.596
260	6.110	8.046	4.125	3.921
280	6.143	8.500	4.269	4.231
298.16	6.143	8.887	4.383	4.504
300	6.144	8.924	4.394	4.530

high temperature heat capacity of rhenium on samples of < 7.5 g. and found, by extrapolation, a mean value over the range 0–20° which is 0.5% lower than the value presented here for that temperature range. They predicted also that the value of  $3R$  for the atomic heat capacity was reached at about –66°. Results presented here

indicate that the value  $3R$  is reached at about  $-51^\circ$ . These small discrepancies are to be expected when high temperature data are used for extensive extrapolations. The estimated accuracy of the integrated entropy values is  $\pm 0.3\%$  above  $200^\circ\text{K.}$ , although the reproducibility of and deviation from the smooth heat capacity *vs.* temperature

plot is somewhat better than this. The entropy below  $20^\circ\text{K.}$  was estimated to be  $0.049 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  by aid of the Debye relation. The molal entropy at  $298.16^\circ\text{K.}$  was calculated to be  $8.89 \pm 0.03 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ .

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## Thermodynamic Properties of Technetium and Rhenium Compounds. V. Low Temperature Heat Capacity and the Thermodynamics of Potassium Perrhenate and the Perrhenate Ion<sup>1</sup>

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RECEIVED JULY 20, 1953

The low temperature heat capacity of potassium perrhenate has been measured from  $16^\circ$  to  $300^\circ\text{K.}$ , and the molal entropy has been calculated to be  $40.12 \pm 0.08 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  at  $298.16^\circ\text{K.}$  When combined with solubility data and heat of solution measurements, the entropy of the perrhenate ion has been found to be  $48.3 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ . The free energy of formation of the ion has been calculated to be  $-167,100 \text{ cal. mole}^{-1}$ .

### Introduction

The molal heat capacity of crystalline potassium perrhenate has been measured from  $16^\circ$  to  $300^\circ\text{K.}$  as part of a study on the thermodynamics of technetium and rhenium. The molal entropy of potassium perrhenate has been calculated from the data. When combined with the solubility measurements of Smith<sup>3</sup> and the calorimetric heats of solution of Roth and Becker,<sup>4</sup> the partial molal entropy of the perrhenate ion can be calculated. This value together with an experimentally determined value for the entropy of rhenium<sup>5</sup> has been used in calculating the thermodynamic functions for the perrhenate ion.

### Experimental

**Materials.**—The potassium perrhenate was furnished by the University of Tennessee and was specified as  $\geq 99.9\%$  pure. The crystals were ground to *ca.* 100–200 mesh, dried at  $100^\circ$  and placed in the calorimeter. The calorimeter was then evacuated to  $10^{-6} \text{ mm.}$ , flushed repeatedly with dry helium, and then sealed at a helium pressure of  $\sim 1/3 \text{ atm.}$  During the measurements it became apparent that an unusual absorption of energy was taking place near  $273^\circ\text{K.}$  After the measurements, the salt was removed and fused. A loss of  $0.30\%$  was observed on the initial fusion, and no further loss occurred upon re-fusion. Since this weight loss corresponded closely to the calculated amount of water which would account for the observed energy involved in the transition ( $0.305\%$ ), it was concluded that drying at  $110^\circ$  and flushing with helium had not been sufficient to remove the water, and the data have been so corrected.<sup>6</sup> The corrected weight of the sample was  $99.5466 \text{ g. (in vacuo)}$ .

(1) This work was performed for the Atomic Energy Commission.

(2) The Radiation Laboratory, University of California, Berkeley, Calif.

(3) W. T. Smith, Jr., *THIS JOURNAL*, **68**, 394 (1946).

(4) W. A. Roth and G. Becker, *Z. physik. Chem.*, **A159**, 27 (1932).

(5) W. T. Smith, Jr., G. D. Oliver and J. W. Cobble, *THIS JOURNAL*, **75**, 5785 (1953); paper IV of this sequence.

(6) The residual water in potassium perrhenate is held very strongly since the sample lost no weight at  $110^\circ$  and did not rapidly lose weight until melting occurred ( $555^\circ$ ). It was further observed that the sample could be heated well above  $273^\circ\text{K.}$ , then cooled as much as 40 degrees below the ice point without causing the transition to occur. Cooling to much lower temperatures for eight hours or so would cause it to reappear.

**Apparatus and Methods.**—The adiabatic cryostat together with the temperature measuring equipment and the energy measuring apparatus has been previously described.<sup>7</sup> The previously calibrated calorimeter was made of copper and was provided with a hole at the top for filling and emptying of the solid. The hole could be capped with a copper disc and sealed with soft solder.<sup>5</sup> Liquid and solid nitrogen and liquid and solid hydrogen were used as the refrigerants.

### Experimental Results

The corrected experimental molal heat capacity data are given in Table I, and the smoothed thermodynamic functions are given in Table II.

TABLE I

OBSERVED MOLAL HEAT CAPACITIES OF $\text{KReO}_4(\text{c})$					
Molecular weight, 289.406; $0^\circ\text{C.} = 273.16^\circ\text{K.}$					
$T_m, ^\circ\text{K.}$	$C_p$	$T_m, ^\circ\text{K.}$	$C_p$	$T_m, ^\circ\text{K.}$	$C_p$
15.94	1.452	75.88	13.759	180.85	23.729
17.14	1.715	80.66	14.426	184.10	23.924
18.37	1.922	82.23	14.630	187.98	24.140
19.95	2.260	86.30	15.222	191.95	24.400
21.55	2.601	90.18	15.736	193.79	24.502
23.60	3.027	93.83	16.170	197.38	24.662
26.26	3.680	97.39	16.657	203.38	25.009
29.13	4.386	103.90	17.369	212.50	25.546
32.38	5.182	113.70	18.416	223.76	26.108
36.36	6.165	121.78	19.258	231.45	26.438
40.80	7.220	129.19	19.885	239.04	26.788
45.76	8.311	137.66	20.696	246.55	27.088
51.30	9.524	145.86	21.381	255.05	27.473
53.07	9.836	151.81	21.997	264.58	28.045
56.66	10.475	161.57	22.504	284.73	28.363
61.07	11.321	170.06	23.061	290.67	29.036
65.84	12.146	179.29	23.656	299.68	29.392

Abnormally high values near  $273^\circ\text{K.}$  due to water have been omitted from Table I. The entropy below  $16^\circ\text{K.}$  was estimated from the Debye relation and amounted to  $0.533 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ . At  $298.16^\circ\text{K.}$  the molal entropy for potassium perrhenate is  $40.12 \pm 0.08 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ . For purposes of calculation we have taken the

(7) G. D. Oliver and J. W. Grisard, *THIS JOURNAL*, **73**, 1688 (1951).